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Barium Molybdenum Selenide Containing Mo_6Se_8 and Mo_9Se_{11} Units: $Ba_2Mo_{15}Se_{19}$

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Abstract. $Ba_2Mo_{15}Se_{19}$, $M_r = 3214{\cdot}02$, trigonal, $R\bar{3}c$, $a_R = 20{\cdot}009\ (3)$ Å, $\alpha_R = 28{\cdot}383\ (4)^\circ$, $V_R = 1599{\cdot}7\ (4)$ Å^3, $Z = 2$, $D_x = 6{\cdot}672$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 293{\cdot}6$ cm^{-1}, $F(000) = 2776$, $T = 295$ K, $R = 0{\cdot}024$ for 960 observed reflections. The title compound is isostructural with $In_2Mo_{15}Se_{19}$ containing monovalent In cations. Its crystal structure is built up from an equal mixture of Mo_6Se_8 and Mo_9Se_{11} cluster units linked together through Mo—Se interunit bonds. The increase of the cationic charge transfer towards the Mo clusters leads to a contraction of both types of clusters along the threefold axis.

Introduction. Low molybdenum oxidation state ternary chalcogenides are often characterized by the occurrence of Mo—Mo bonds leading to clearly defined bonded groups called clusters. For instance, the tetrahedral Mo_4 and the octahedral Mo_6 clusters were first observed in compounds with general formula MMo_4X_8 (M = Al, Ga; X = S, Se, Te) (Vandenberg & Brasen, 1975) and $M_xMo_6X_8$ (M = 3d, Na, K, Ca, Sr, Ba, Sn, Pb, RE . . .) (Chevrel & Sergent, 1982). More recently, the condensed clusters Mo_9, Mo_{12}, Mo_{15}, Mo_{18}, Mo_{24} and Mo_{30} resulting from the face-sharing of n Mo_6 octahedra (n = 2, 3, 4, 5, 7 and 9) were obtained by lowering the non-metal/metal ratio (X/M) below 8:6 and taking large metal cations (Rb^+, Cs^+) as the ternary element in compounds of general formula $M_{n-2}Mo_{3n}X_{3n+2}$ (Gougeon, 1984; Gougeon, Potel, Padiou & Sergent, 1987, 1988). Smaller cations [$r(M) < 1{\cdot}35$ Å] usually lead to the formation of the Mo_6 materials. Whereas all of these condensed clusters have been found alone (*i.e.* one type of cluster) in the compounds above, the Mo_9 and Mo_{12} clusters were also found to cocrystallize with the Mo_6 cluster in $In_2Mo_{15}Se_{19}$ (Potel, Chevrel & Sergent, 1981) and $Tl_2Mo_9S_{11}$ (Potel, Chevrel & Sergent, 1980) respectively.

In this paper, we describe the X-ray crystal structure of the first condensed-cluster compound containing a divalent cation and belonging to the $In_2Mo_{15}Se_{19}$ structural type: $Ba_2Mo_{15}Se_{19}$.

Experimental. Single crystals of $Ba_2Mo_{15}Se_{19}$ were obtained by heating a cold-pressed pellet of a stoichiometric mixture of BaSe, $MoSe_2$ and Mo in sealed molybdenum crucibles at 1973 K for one hour and then cooling it to 1273 K at a rate of 100 K h^{-1}.

A crystal fragment with dimensions 0·1 × 0·1 × 0·11 mm was selected for intensity data collection carried out on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with $10 \leq 2\theta \leq 32^\circ$. 2136 reflections were recorded in the range $2 \leq 2\theta \leq 60^\circ$ with h: $-28 \rightarrow 28$, k: $-28 \rightarrow 28$, l: $0 \rightarrow 28$, $k > h$ and $|l| > |k|$ (rhombohedral setting); ω–2θ mode was

Table 1. *Positional parameters and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Mo(1)	0·50036 (3)	0·68563 (3)	0·37266 (3)	0·55 (1)
Mo(2)	0·22126 (3)	0·05024 (3)	0·36063 (3)	0·55 (1)
Mo(3)	0·40815 (9)	$1-x$	0·250	0·54 (1)
Se(1)	0·19270 (3)	0·80154 (3)	0·55685 (3)	0·72 (1)
Se(2)	0·53266 (3)	0·92095 (3)	0·18783 (3)	0·73 (2)
Se(3)	0·0569 (1)	$1-x$	0·750	0·81 (1)
Se(4)	0·44519 (2)	x	x	0·875 (5)
Se(5)	0·17544 (2)	x	x	0·814 (5)
Ba	0·38494 (2)	x	x	1·728 (4)

Table 2. *Selected interatomic distances* (Å)

[Mo(1)—Mo(1)]$_\Delta$	2 × 2·6741 (11)	[Mo(2)—Mo(2)]$_\Delta$	2 × 2·6418 (11)
Mo(1)$_\Delta$—Mo(1)$_\Delta$	2 × 2·7269 (10)	[Mo(3)—Mo(3)]$_\Delta$	2 × 2·6874 (8)
		Mo(2)$_\Delta$—Mo(3)$_\Delta$	2·6922 (18)
			2·7803 (16)
Δ(1)—Δ(1)	2·257	Δ(2)—Δ(3)	2·263
Mo(1)—Se(4)	2·5502 (7)	Mo(2)—Se(5)	2·5395 (7)
Mo(1)—Se(1)	2·5636 (9)	Mo(2)—Se(2)	2·5897 (9)
	2·5966 (10)		2·6342 (9)
	2·6182 (10)	Mo(2)—Se(3)	2·7096 (20)
Mo(1)—Se(2) (interunit)	2·6027 (9)	Mo(2)—Se(1) (interunit)	2·6799 (9)
Ba—Se(2)	3 × 3·2424 (7)	Mo(3)—Se(2)	2·5472 (13)
Se(4)	3·4689 (5)	Mo(3)—Se(3)	2·6084 (6)
Se(5)	3·4761 (5)	Mo(1)—Mo(2) (intercluster)	3·4721 (8)
Se(1)	3 × 3·7235 (7)		
Se(3)	3 × 3·8659 (5)		

Notes. [Mo—Mo]$_\Delta$: distance between Mo atoms related through the threefold axis and thus forming an Mo_3 triangle perpendicular to the latter, also called intratriangle distance in the text. Mo$_\Delta$—Mo$_\Delta$: distance between Mo atoms of different Mo_3 triangles and called intertriangle distance.

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used with scan width $\Delta\omega = (0{\cdot}8 + 0{\cdot}35\mathrm{tg}\theta)^\circ$ and counter aperture $\Delta l = (2 + 0{\cdot}5\mathrm{tg}\theta)$ mm. Three orientation and three intensity control reflections were checked every 250 reflections and every hour, respectively, and showed no significant variation. Data were corrected for Lorentz–polarization and an empirical absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to isotropically refined data. The minimum and maximum correction factors were 0·929 and 1·069. After averaging of the symmetry-related reflections ($R_{\rm int} = 0{\cdot}034$), 1371 unique reflections of which 960 had $I \geq 2\sigma(I)$ were used to solve the structure.

The atomic coordinates of $\mathrm{In_2Mo_{15}Se_{19}}$ (Potel *et al.*, 1981) were used as initial values in the first stage of the structure refinement. Subsequently, isotropic and anisotropic thermal parameters for all atoms as well as the extinction coefficient were introduced in the full-matrix least-squares refinement on F. The final values of R and wR were 0·024 and 0·026 respectively, where $w = 4F_o^2/[\sigma^2(F_o^2) + (0{\cdot}02F_o^2)^2]$ and $S = 1{\cdot}15$ using 960 reflections with $I \geq 2\sigma(I)$ and 57 variables. The largest shift/e.s.d. was $<0{\cdot}01$ and the largest residuals on final difference map were 0·96 and $-1{\cdot}12$ e Å^{-3}; final value of $g = 8{\cdot}81 \times 10^{-8}$ (Stout & Jensen, 1968). Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). All the calculations were performed on a PDP 11/60 with the *SDP* programs (B. A. Frenz & Associates Inc., 1985). Final atomic coordinates and equivalent isotropic thermal parameters with their e.s.d.'s are given in Table 1 and selected interatomic distances in Table 2.*

Discussion. The three-dimensional packing of the $\mathrm{Mo_6Se_8}$ and $\mathrm{Mo_9Se_{11}}$ cluster units is shown in Fig. 1. Both cluster units are obviously geometrically identical to those found in $\mathrm{In_2Mo_{15}Se_{19}}$. Thus the $\mathrm{Mo_6Se_8}$ unit consists of an $\mathrm{Mo_6}$ octahedron inscribed in a pseudo-cube $\mathrm{Se_8}$ and the $\mathrm{Mo_9Se_{11}}$ of a two-face-linked $\mathrm{Mo_6}$ octahedron surrounded by 11 Se atoms in the same way as the single $\mathrm{Mo_6Se_8}$ unit. However, both types of cluster display various Mo—Mo bond lengths that reflect the different cationic charge transfer towards the metal-atom clusters in the two parent compounds. Consequently, all the Mo—Mo distances within the $\mathrm{Mo_6}$ cluster are shorter in $\mathrm{Ba_2Mo_{15}Se_{19}}$ than in $\mathrm{In_2Mo_{15}Se_{19}}$ in which the Mo(1)—Mo(1) intra- and intertriangle distances are 2·686 (2) and 2·772 (10) Å respectively. This contraction of the $\mathrm{Mo_6}$ cluster is well illustrated in particular by the interplane distance $\Delta(1)$—$\Delta(1)$ which decreases from 2·30 Å in $\mathrm{In_2Mo_{15}Se_{19}}$ to 2·257 Å in $\mathrm{Ba_2Mo_{15}Se_{19}}$. A similar behavior is also observed for the $M\mathrm{Mo_6}X_8$ series when the cationic charge increases (Yvon, 1979). The structural response of the $\mathrm{Mo_9}$ cluster with respect to the increase of the charge transfer is more complex. However, the $[\mathrm{Mo(2)—Mo(2)}]_\Delta$ intratriangle as well as the two $\mathrm{Mo(2)}_\Delta$—$\mathrm{Mo(3)}_\Delta$ intertriangle distances are shorter in the barium compound [2·673 (2) and 2·712 (5), 2·808 (6) Å respectively in $\mathrm{In_2Mo_{15}Se_{19}}$]. On the other hand, a slight increase of the Mo(3)—Mo(3)

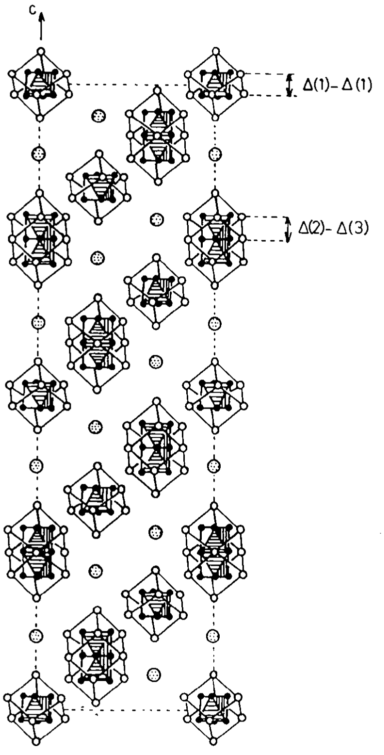

Fig. 1. Projection of the structure of $\mathrm{Ba_2Mo_{15}Se_{19}}$ on the hexagonal (11$\bar{2}$0) plane. Filled circles: Mo atoms; empty circles: Se atoms; dotted circles: Ba atoms.

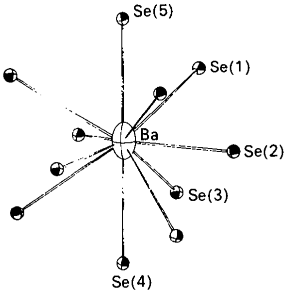

Fig. 2. The coordination polyhedron of the Ba atoms.

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* Lists of structure factors, anisotropic thermal parameters and bond distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51915 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bonds occurs in the median Mo_3 triangle [2·680 (4) Å in $In_2Mo_{15}Se_{19}$]. Nevertheless, the overall effect is again a contraction of the cluster as reflected by the interplane distance $\Delta(2)$—$\Delta(3)$ which decreases from 2·280 to 2·263 Å. This trend is analogous to that reported for the series $In_xMo_{15}Se_{19}$ ($2\cdot9 \leq x \leq 3.4$) when the indium content x increases (Grüttner, Yvon, Chevrel, Potel, Sergent & Seeber, 1979; Potel, 1981). The latter compound also contains Mo_6Se_8 and Mo_9Se_{11} units but arranged in a different way. The Mo—Se distances are nearly unaffected by the cationic charge and range between 2·5395 (7) and 2·710 (2) Å as usual.

The Ba atoms, located in channels running along the a axis of the rhombohedral unit cell, are each surrounded by 11 Se atoms. The five closest Se atoms at distances ranging from 3·2424 (7) to 3·4761 (5) Å form a trigonal bipyramid, with Se(4) and Se(5) located on the threefold axis in axial positions and three related Se(2) in the equatorial sites. The other six [three Se(1) and three Se(3)] cap the faces of the bipyramid with Ba–Se distances between 3·7235 (7) and 3·8659 (5) Å (Fig. 2). Whereas in the title compound the Ba atom is nearly equidistant from the two axial Se atoms, in $In_2Mo_{15}Se_{19}$ the In is slightly displaced towards the Se(4) atoms [In—Se(4) 3·468 (6) and In—Se(5) 3·593 (6) Å] probably owing to the presence of the lone pair. This effect is still more evident in $Tl_2Mo_{15}Se_{19}$ (Potel & Gougeon, 1987) where the Tl—Se(4) and Tl—Se(5) distances are 3·379 and 3·684 Å respectively.

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Structural Characterization of $WCl_6.S_8$

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Abstract. Tungsten hexachloride-*cyclo*-octasulfur, (1), $M_r = 653\cdot08$, triclinic, $P\bar{1}$, $a = 7\cdot901$ (1), $b = 7\cdot923$ (1), $c = 12\cdot696$ (2) Å, $\alpha = 97\cdot08$ (1), $\beta = 100\cdot50$ (1), $\gamma = 90\cdot26$ (1)°, $V = 775\cdot2$ (4) Å^3, $Z = 2$, $D_x = 2\cdot798$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 96\cdot65$ cm^{-1}, $F(000) = 608$, $T = 294$ K, $R = 0\cdot028$ for 1337 observed reflections. The asymmetric unit is composed of one molecule of WCl_6 in which the W atom sits at the center of a nearly perfect octahedron of Cl atoms, and one molecule of S_8 which adopts the crown ring structure. The average W—Cl distance is 2·276 (2) Å, the average S—S distance 2·044 (1) Å, and the average S—S—S angle 107·9 (1)°.

Introduction. During the course of a synthetic program directed towards the preparation of mixed metal chalcogenide halide clusters we have inadvertently prepared WCl_6S_8. The structure determination we report here complements that for WCl_6 (Ketelaar & van Oosterhout, 1943).

Experimental. A Pyrex tube evacuated to 2×10^{-4} torr ($2\cdot67 \times 10^{-2}$ Pa), containing Ti (0·30 g,

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